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(54) Title: NOVEL FLAME RETARDANT PLASTICIZERS

(57) Abstract

The present invention provides novel esters synthesized from organic alcohols and tetrahalophthalic anydride or tetrahalophthalic acid, processes to make such esters, and novel uses of these esters. The invention provides three Groups of dialkyltetrahalophthalate compositions which exhibit surprisingly advantageous features, including excellent plasticizing functionality and low smoke generation. The esters may be symmetrical, in that both alcohols of the ester are the same, or they may be unsymmetrical with both alcohols of the derived phthalate ester different, or they may be mixtures of symmetrical and unsymmetrical esters. Inventive esters are useful as flame–retardant plasticizers in PVC or other polymeric systems.

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NOVEL FLAME RETARDANT PLASTICIZERS

REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/049,900, filed June 18, 1997 and entitled MATERIALS, PROCESSES FOR MANUFACTURING AND APPLICATIONS FOR TETRABROMOPHTHALATE ESTERS, which is hereby incorporated by reference herein in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to novel flame retardant plasticizers synthesized from organic alcohols and tetrahalophthalic anhydride or tetrahalophthalic acid, processes to make such plasticizers, and uses of these plasticizers. Inventive materials are esters derived from (1) tetrahalophthalic anhydride or tetrahalophthalic acid and (2) linear organic alcohols, or mixtures of linear and branched organic alcohols, in the presence of a catalyst in a one-pot reaction. The esters may be symmetrical, in that both alcohols of the ester are the same, or they may be unsymmetrical with both alcohols of the derived phthalate ester different, or they may be mixtures of symmetrical and unsymmetrical esters. Inventive esters are useful as flame-retardant plasticizers in PVC or other polymeric systems.

Discussion of Related Art

Poly(vinyl chloride), hereafter referred to as PVC, is extensively used in wire insulation and sheathing for electric cables because of its ready availability, mechanical toughness, low cost, resistance to chemicals and weathering, and good dielectric properties. A broad range of electrical conductors and electrical cables are installed in modern buildings for a wide variety of uses, including, for example, data transmission between computers, voice communications, as well as control signal transmission for building security, fire alarm, and temperature control systems. These

cable networks extend throughout modern office and industrial buildings, and frequently extend through the space between the dropped ceiling and the floor above.

In use, PVC is almost always plasticized to overcome its natural rigidity and permit it to be processed into a flexible material. In addition, other additives such as thermal stabilizers, lubricants, pigments, fillers, impact modifiers, and flame retardants are generally employed to produce PVC compositions having desired properties. Unmodified PVC is thermally unstable, decomposing at about 150°C to release HCl and produce sites of unsaturation in the polymer which lead to chain crosslinking and scission, resulting in degradation of the polymer's properties. As the PVC decomposes, the resin becomes discolored, brittle, and finally insoluble. To improve thermal stability, various thermal stabilizers are nearly always employed in PVC compositions. The stabilizers generally used are metallic salts of inorganic and organic acids and phenols, organometallics, epoxy compounds, and phosphates. In wire and cable applications, lead stabilization systems are widely used.

Despite its thermal instability, unmodified PVC has relatively good flame retardant properties due to its high chlorine content. However, the plasticizer necessary for flexibility and good processing properties generally increases the flammability of PVC compositions, especially if used at high levels. Moreover, when PVC burns, it produces considerable smoke, and the addition of flame retardant materials to plasticized compositions to reduce their flammability generally increases smoke generation upon burning. Smoke is particularly dangerous since it not only contains toxic by-products of combustion and thermal decomposition of the plastic, but also restricts visibility and disorients potential victims, resulting in panic.

The plastics industry has long recognized that use of PVC in interior furnishings, building materials, and coverings for wire and cable presents the hazards of flame, toxic decomposition products, and smoke in the event of fire, as discussed above. It has therefore expended very considerable efforts to find additives for PVC which reduce thermal decomposition, flammability, and smoke in the event that such PVC compositions are subjected to high temperature or flame.

Such research has yielded knowledge of several classes of additives, such as, for example, stabilizers, flame retardants, smoke suppressants and plasticizers, which function in PVC, and has disclosed many useful individual chemical compounds

within those classes, but further improvements are needed to optimize the degree of flame retardency and plasticizing functionality, while minimizing smoke generation. For example, tetrahalophthalates and related compounds are known flame-retardants, as well as plasticizers in various applications, such as in the formation of polymeric compositions used for forming primary insulation and protective jacketing for electrical conductors. Thus, Coaker et al. (U.S. Pat. No. 5,036,121 uses brominated phthalic acid esters together with polyvinyl chloride. These compounds may also be used for imparting enhanced flame resistance to wool (U.S. Patent No. 4,277,379). The disclosures of these references and of the other publications and patents referred to herein are incorporated herein by reference.

The process for preparation of tetrahalophthalates as known in the art utilizes halophthalic anhydrides or acids, and the process for the preparation of dialkyltetrahalophthalates by reacting a tetrahalophthalic anhydride with an alkanol in the presence of a lower tetraalkyl titanate as is well known in the art. Numerous processes have been described for the preparation of dialkyl phthalates by esterification of various alcohols with phthalic anhydride or acid in the presence of acidic catalysts, such as sulfuric acid, phosphoric acid, toluene sulfonic acid, and methane sulfonic acid. Sagara et al. (U.S. Patent No. 4,284,793) discloses a method for producing plasticizers, in which phthalic anhydride is reacted with an alcohol in the presence of a titanate catalyst. The resultant ester is treated with a solid alkali, such as sodium carbonate, and adsorbing agent(s) in the absence of water. Mamuzic et al. (U.S. Patent No. 4,754,053) discloses the preparation of tetrabromophthalate diesters using sodium carbonate decahydrate as an essential part of the process.

In view of the above, there is a continued need in the relevant field for improved compositions for improving flame retardency and plasticizing functionality while minimizing smoke generation. The present application addresses this need and provides dialkyltetrahalophthalates having relatively large alkyl groups or having a mixture of linear and branched alkyl groups. With respect to the former, it is believed that the absence of such compositions in the prior art is due, at least in part, to the general belief that an increase in the number of carbons therein would result in unacceptable levels of smoke generation, a decidedly disadvantageous feature. With respect to the latter, its absence in the prior art may be attributable to the fact that the

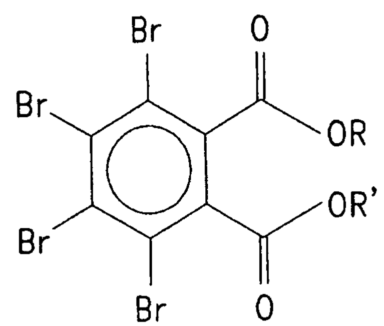
literature indicates that the presence of branched alkyl groups therein reduces the efficacy of the composition as a plasticizer.

The present invention, however, provides a variety of dialkyltetrahalophthalates having relatively high-carbon alkyl groups and dialkyltetrahalophthalates having linear and branched-chain alkyl groups, these compositions exhibiting the excellent features described herein.

SUMMARY OF THE INVENTION

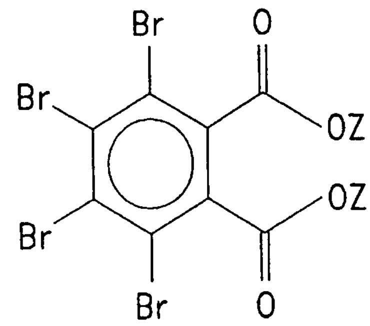
The present invention provides flame retardant plasticizers having favorably low smoke generation features and having excellent plasticizing features. Also provided are flame retardant plasticizers that are more cheaply made and used than alternative plasticizers disclosed in the prior art and which exhibit excellent plasticizing features. Also provided are excellent polymer formulations featuring flame retardant plasticizers selected in accordance with the invention.

In one aspect of the invention, there is provided a flame retardant plasticizer composition, comprising a tetrabromophthalate ester having the formula:



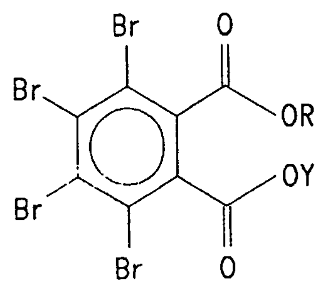
wherein R is a first linear alkyl chain of from about 5 to about 16 carbons; wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons; wherein R' is different than R; and wherein one of R and R' comprises at least seven carbons. It is also a feature of the invention that a tetrachlorophthalate ester may be combined with the tetrabromophthalate ester in inventive compositions described herein to provide excellent flame retardant plasticizers.

In another aspect of the invention, there is provided a flame retardant plasticizer composition, comprising a tetrabromophthalate ester having the formula:



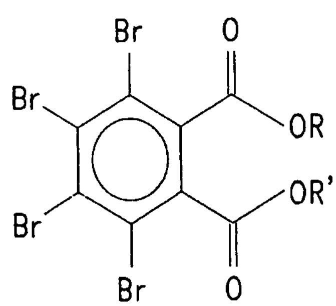
wherein Z is a linear alkyl chain of from about 14 to about 16 carbons.

In an alternate aspect of the invention, there is provided a flame retardant plasticizer composition, comprising a tetrabromophthalate ester having the formula:



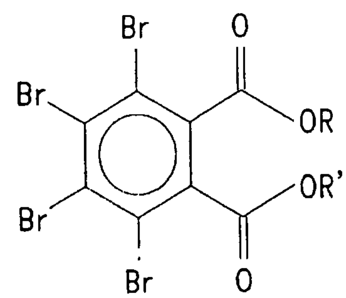
wherein R is a linear alkyl chain of from about 5 to about 16 carbons; and wherein Y is a branched alkyl chain of from about 5 to about 16 carbons.

Also provided by the invention is a formulation comprising a polyvinyl chloride; a heat stabilizer; a lubricant; and a composition comprising a tetrabromophthalate ester having the formula:



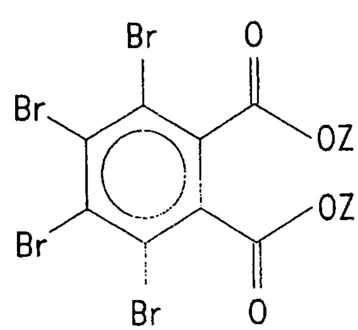
wherein R is a first linear alkyl chain of from about 5 to about 16 carbons; wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons; wherein R' is different than R; and wherein the total number of carbons in R and R' is greater than 12.

Also provided by the invention is a formulation comprising a polyvinyl chloride;
a heat stabilizer; a lubricant; and a composition comprising a tetrabromophthalate ester having the formula:



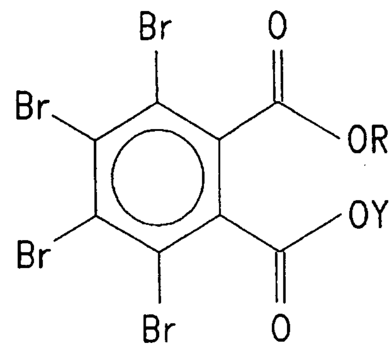
wherein R is a first linear alkyl chain of from about 5 to about 16 carbons; wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons; wherein R' is different than R; and wherein one of R and R' comprises at least seven carbons.

In another aspect of the invention, there is provided a formulation comprising a polyvinyl chloride; a heat stabilizer; a lubricant; and a composition comprising a tetrabromophthalate ester having the formula:



wherein Z is a linear alkyl chain of from about 14 to about 16 carbons.

In another aspect of the invention, there is provided a formulation comprising a polyvinyl chloride; a heat stabilizer; a lubricant; and a composition comprising a tetrabromophthalate ester having the formula:



wherein R is a linear alkyl chain of from about 5 to about 16 carbons; and wherein Y is a branched alkyl chain of from about 5 to about 16 carbons.

In another aspect of the invention, there is provided a flame retardant plasticizer composition, comprising a tetrabromobenzoate ester comprising an alkyl chain of from about 5 to about 16 carbons.

It is an object of the present invention provide a variety of novel tetrahalophthalate esters that exhibit excellent plasticizing features and also reduced smoke generation and/or improved physical properties. Further objects, advantages and features of the present invention will be apparent from the detailed description herein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For purposes of promoting an understanding of the principles of the invention, reference will now be made to particular embodiments of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the invention, and such further applications of the principles of the invention as described herein being contemplated as would normally occur to one skilled in the art to which the invention pertains.

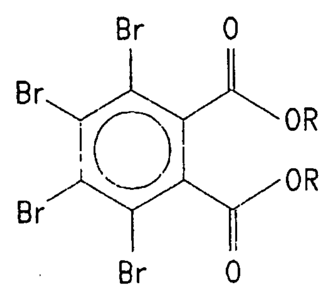
The invention relates generally to esters of tetrahalophthalate, and, more specifically to three classes of tetrahalophthalate esters. Regarding tetrahalophthalates in general, it is well known that they may be made by providing a tetrahalophthalic compound selected from the group consisting of tetrahalophthalic anhydrides and tetrahalophthalic acids, and reacting the same with an alkanol, preferably in the presence of an acid catalyst. With respect to the tetrabromophthalic compound, the anhydride is more readily available and therefore is the most preferred form. It is also contemplated herein that a tetrachlorophthalic compound may be mixed with a tetrabromophthalic compound in certain preferred aspects of the invention. With respect to the alkanol, linear alkanols are typically used in known processes, such as the processes described in U.S. Patent No. 5,049,697 or U.S. Patent No. 5,308,366, for example. The tetrahalophthalic compound is esterified with a catalyst which may be, for example, an alkyl titanate catalyst, zirconium tetrabutoxide or tin oxalate.

In the invention, the tetrahalophthalic compound is reacted with an excess of alkanol, as is known in the art, to form a reaction mass. In one aspect of the invention, there are provided dialkyltetrabromophthalate compositions referred to herein as Group 1 compositions. The alkanol used to make Group 1 compositions is a mixture of two different alkanols, each having from 5 to 16 carbons. Preferably, at least one of the alkanols has at least seven carbon atoms. The alkanol mixture may be prepared, for example, from Oxo and Ziegler manufacturing processes as known in the art (see Weissermel, K. and Arpe, H-J., *Industrial Organic Chemistry,* pages 132-134, 206-208, VCH Publishers, New York, 1978). Alternatively, the alkanol mixture may be prepared by providing two alkanols of the desired composition and mixing them in a desired proportion. The mixture preferably comprises a ratio of two

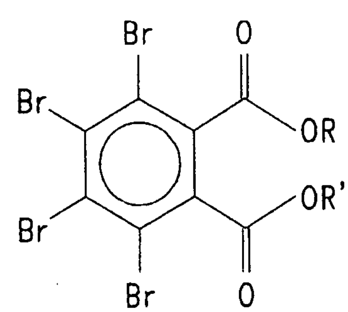
alkanols of from about 1:10 to about 10:1, more preferably from about 1:8 to about 8:1, and most preferably from about 5:1 to about 1:5. In one preferred aspect of the invention, the mixture comprises hexanol and an alkanol selected from the group consisting of octanol, decanol and dodecanol. In another preferred aspect of the invention, the mixture comprises octanol and an alkanol selected from the group consisting of decanol and dodecanol. In another preferred aspect of the invention, the mixture comprises decanol and dodecanol. It is, of course, not intended that this aspect of the invention be limited to these exemplary mixtures.

In this aspect of the invention, the tetrabromophthalate ester reaction product comprises a mixture of the following three compounds:

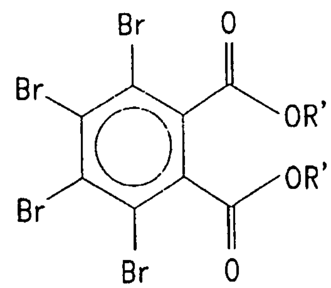
Compound 1



Compound 2



Compound 3



wherein R is a first linear alkyl chain of from 5 to about 16 carbons, wherein R' is a second linear alkyl chain of from 5 to about 16 carbons, and wherein R' is different than R. While the three compounds may be separated prior to use in accordance with the invention, a mixture of the three compounds shown above may be advantageously used as an excellent flame retardant plasticizer, as described below. It is seen that the ratio of the three compounds in the reaction product will depend upon the ratio of alkanols in the alkanol mixture. Surprisingly, it has been found that the ratio of the products may be predicted by use of the following formula

$$(\alpha[ROH] + \beta[R'OH])^k$$

where α is the mole fraction of alcohol ROH in the alkanol mix, where β is the mole fraction of alkanol R'OH in the alkanol mix, k is the number of reactive sites on the acid or anhydride being esterified, and where the powers associated with [ROH] and [R'OH] denote the number of alkanol molecules attached to the anhydride or acid as esters. For example, where the reactant is tetrabromophthalic anhydride, the number of reactive sites is 2 and therefore k=2, where the alkanol molar ratio is 3:1 the molar fractions are α=0.75 and β=0.25 and the equation simplifies to:

$$0.5625[ROH]^2 + 0.375[ROH]*[R'OH] + 0.0625[R'OH]^2$$

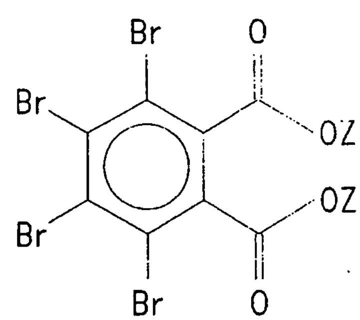
or

$$9[ROH]^2 + 6[ROH]*[R'OH] + 1[R'OH]^2$$

In other words, where the alkanol ratio is 3:1, the ratio of compound 1 to compound 2 to compound 3 will be about 9:6:1. In a particular preferred aspect of the invention, the alkanol mixture starting material comprises a ratio of octanol to decanol of about 3:1, and the tetrabromophthalate ester reaction product comprises a ratio of dioctyltetrabromophthalate:octyl-decyltetrabromophthalate:didecyltetrabromophthalate of about 9:6:1. These equations hold provided that alcohol removal processes such as byproduct formation, for example ether or olefin formation, or alcohol removal processes, such as selective volatilization, do not change the alkanol molar ratios. It is not intended that the invention be limited to such specific ratios.

In a second aspect of the invention, relating to dialkyltetrabromophthalate compositions referred to herein as Group 2 compositions, the alkanol used is an alkanol having from about 14 to about 16 carbons. In this aspect of the invention, the tetrabromophthalate ester reaction product has the following formula:

Compound 1



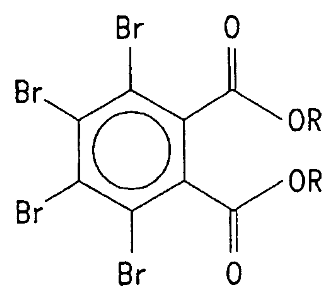
wherein Z is a linear alkyl chain of from about 14 to about 16 carbons.

In a third aspect of the invention, relating to dialkyltetrabromophthalate compositions referred to herein as Group 3 compositions, the alkanol used is a mixture of two different alkanols, each having from about 5 to about 16 carbons, wherein one of the alkanols is a linear alkanol and the other is a branched chain alkanol. The mixture preferably comprises a ratio of the two alkanols of from about 1:10 to about 10:1, more preferably from about 1:8 to about 8:1, and most preferably

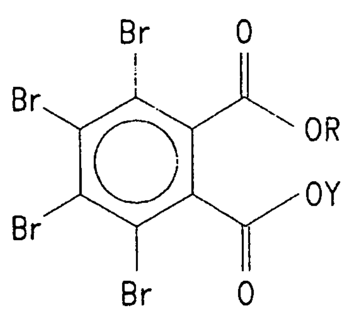
from about 5:1 to about 1:5. In one preferred aspect of the invention, the branched chain alkanol is ethylhexanol.

In this aspect of the invention, the tetrabromophthalate ester reaction product comprises a mixture of the following three compounds:

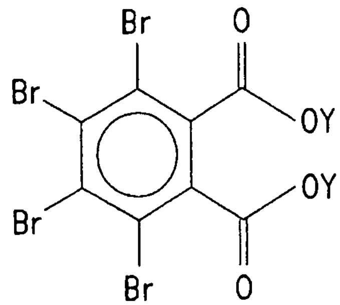
Compound 1



Compound 2



Compound 3



wherein R is a linear alkyl chain of from 5 to about 16 carbons, and wherein Y is a branched alkyl chain of from about 5 to about 16 carbons. While the three compounds may be separated prior to use in accordance with the invention, a mixture of the three compounds shown above may be advantageously used as an excellent flame retardant plasticizer, as described below. It is seen that the ratio of the three compounds in the reaction product will depend upon the ratio of alkanols in the alkanol mixture. For example, as described above, where the alkanol ratio is 3:1, the ratio of compound 1 to compound 2 to compound 3 will be about 9:6:1. More typically, commercially available branched alkanols are themselves mixtures of alkanols. For example, Exxal 8, isooctyl alcohol available from Exxon Chemical, is a mixture of dimethyl-1-hexanols and methyl-1-heptanols. In these cases, the ratio of products can be calculated from the following equation:

$$(\alpha[ROH] + \beta[R'OH] + \chi[R'OH] + \delta[R'''OH] + \ldots + \zeta[R''''''OH]^{k}$$

where the Greek letters stand for the mole fractions of each component of the alcohol mixtures, for example, where α is the molar fraction of alcohol ROH in the alkanol mix and where β is the mole fraction of alkanol R'OH in the alkanol mix, etc.; [ROH], [R'OH], [R''OH], etc. stand for the alkanols in the mixture, k is the number of reactive sites on the acid or anhydride being esterified, and where the powers associated with [ROH] and [R'OH] denote the number of alkanol molecules attached to the anhydride or acid as esters. This equation reduces to the simple equation on page 11 provided that the branched alcohol consists of only one component.

Dialkyltetrahalophthalate compounds of Groups 1, 2 and 3 find advantageous use as flame retardant plasticizers in polymer formulations such as, for example, poly (vinyl chloride) (PVC) formulations and polyethylene systems. Thus another aspect of the invention is a polymer formulation comprising a base polymer and a flame retardant plasticizer of Group 1, Group 2 or Group 3 (in the case of Groups 1 and 3, the flame retardant plasticizer may be a mix of the dialkyltetrabromophthalate compounds found in the reaction product or may be an isolated dialkyltetrabromophthalate compound). As a specific example of an inventive formulation, there is provided a formulation comprising a PVC, a heat stabilizer, a lubricant and a flame retardant plasticizer selected from a Group 1 plasticizer, a Group 2 plasticizer and a Group 3 plasticizer. There may also be present a wide variety of optional ingredients in an inventive formulation, including, for example, chlorinated polyvinyl chloride (CPVC), a smoke suppressant, one or more filler materials and antimony trioxide. It is well known that a number of ingredients may be present for the end use of the formulation, such as, for example, an ultraviolet stabilizer, which will not necessarily be present in an intermediate formulation. The present invention encompasses the intermediate formulations as a useful aspect thereof.

The heat stabilizer may be selected from a wide variety of compositions known in the art, many of which are widely known, including, for example, tribasic lead sulfate, dibasic lead phthalate, dibasic lead phosphite, lead sulfophthalate and basic lead sulfophthalate. An exemplary commercial heat stabilizer is Tribase XL by Cookson Chemicals. The lubricant may also be selected from a wide variety of compositions known in the art, including, for example, stearic acid, bled of paraffin wax and calcium, stearate, and paraffin wax. An exemplary commercial lubricant is Petrac 270 by Synthetic Products. A smoke suppressant advantageously used in accordance with the invention may be selected from a variety of compositions known in the art, including, for example, ammonium octamolybdate and zinc molybdate. An exemplary commercial smoke suppressant is AOM by Climax Molybdenum. A wide variety of filler materials may be used, such as, for example, alumina trihydrate, calcined aluminum silicate and electrica grade clay. An exemplary commercial filler is Solem 932 by Solem Industries. Examples of ultraviolet stabilizers include, for

example, hindered amine light stabilizers and UV absorbers. An exemplary commercial ultraviolet stabilizer is Lowilite 76 by Great Lakes Chemical Corporation.

While the invention encompasses a wide variety of formulations as described above, some exemplary formulations are set forth in the examples. With respect to these exemplary formulations, the ingredients are commercially available materials, the identities of which are described below:

(1) GEON 102 EP is a high viscosity, high molecular weight PVC, Chemical Abstracts Registry No. 9002-86-2 available from the B.F. Goodrich Company;

(2) An example of a suitable chlorinated poly(vinyl chloride) ("CPVC") is TEMPRITE 627X563, available from B.F. Goodrich Company;

(3) Elvaloy 741 is a plasticizer which is a terpolymer of acrylic acid, ethylene, and vinyl acetate, Chemical Abstracts Registry No. 26713-18-8, available from DuPont;

(4) An example of a suitable tribasic lead is TRIBASE, Chemical Abstracts Registry No. 12202-17-4, which is a heat stabilizer available from Associated Lead, Inc.;

(5) Ammonium octamolybdate ("AOM") is a smoke suppressant having a Chemical Abstracts Registry No. 12411-64-2, available from Climax Molybdenum;

(6) Alumina trihydrate ("ATH") is a flame retardant and smoke suppressant; and SOLEM 932 is an ATH having a Chemical Abstracts Registry No. 21645-51-2, available from Solem Industries;

(7) Topanol CA is an antioxidant having the chemical name 4,4,4"-(1-methyl-1-propanyl-3-ylidene)tris(2-(1,1-dimethyl-ethyl))-5-methyl phenol, having the Chemical Abstracts Registry No. 1843-03-4, available from ICI America;

(8) Stearic acid is a lubricant having the Chemical Abstracts Registry No. 57-11-4, available from Synthetic Products, Inc.;

(9) An example of a dibasic lead stearate lubricant is DS 207, Chemical Abstracts Registry No. 56189-09-4, available from Associated Lead, Inc.;

(10) Aristowax 165 is a paraffin wax lubricant having the Chemical Abstracts Registry No. 8002-74-2, available from the Ross Corporation;

(11) Dioctyl sebacate is a plasticizer having the Chemical Abstracts Registry No. 122-62-3, available from the C.P. Hall Company;

(12) LSFR antimony trioxide is a low smoke flame retardant having the Chemical Abstracts Registry No. 1309-64-4, available from Lauryl Industries. While the above are described for purposes of example, it is understood that this list is not intended to be limiting, but only to provide examples of ingredients in certain inventive formulations.

As shown in the examples, inventive formulations exhibit excellent plasticizing characteristics, especially at low temperatures. These characteristics are represented by Glass Transition data (T_g) and DMA Onset data. Generally, the more linear carbons on the ester alkyl group, the better the low temperature properties in the simple formulations of examples 20-27. Surprisingly, materials which nominally contain the same number of linear carbon atoms on the sidechains do not have the same T_g. It has been found that the distribution of products in the mixtures affects the T_g. It is preferred in simple formulations to maximize the distribution of materials in the flame retardant mix which have more carbon atoms, especially longer linear carbon chains. The complex formulations of examples 28-30 behave differently. Here, surprisingly, a higher number of linear carbon atoms does not necessarily lead to a lower DMA Onset or Peak Storage Modulus. It has also been surprisingly found that Group 1 and Group 2 compositions have advantageously low smoke generation with smoke generation in both flaming and radiant modes in complex formulations.

In view of the above, inventive formulations find advantageous use in a wide variety of systems which currently utilize PVC formulations and polyethylene formulations, such as, for example, the wire and cable industry and the construction industry. Inventive formulations exhibit excellent low temperature properties, such as, for example, low temperature flexibility and resistance to cracking.

In another aspect of the invention, inventive principles are applicable to benzoate compounds, in addition to phthalate compounds. Thus, tetrahalobenzoate compounds esterified using higher alkanols, such as branched or unbranched C7-C16 alkanols, are expected to have the advantageous features of phthalate compounds specifically described herein, and are included within the scope of the invention. Surprisingly, the tetrahalobenzoate/tetrahalophthalate plasticizers of this invention show improved low temperature performance over tetrahalophthalates having the

same number of total linear carbon atoms on the ester functionality as shown in examples 28 and 29.

In a further aspect of this invention, inventive principles are applicable to mixtures of linear tetrabromophthalate esters and tetrachlorophthalate esters. Thus, tetrachlorophthalic anhydride or tetrachlorophthalic acid may be esterified with higher alkanols, such as branched or unbranched C7 to C16 alkanols, either in the presence of a tetrabromophthalic anhydride or tetrabromophthalic acid or the tetrachlorophthalate esters can be made in a separate step and then mixed with a tetrabromophthalate ester, to give a mixture containing both tetrachlorophthalate esters and tetrabromophthalate esters. These are useful low temperature plasticizers for PVC. The preferred embodiment is to use the chlorophthalate esters to maintain a liquid product, especially when mixed with low melting tetrabromophthalate esters or tetrabromobenzoates.

The invention will be further described with reference to the following specific Examples. It will be understood that these Examples are illustrative and not restrictive in nature.

EXAMPLE ONE
Hexyl octyl tetrabromophthalate

Tetrabromomphthalic anhydride (421.1 g), sodium carbonate (0.60 g), n-hexanol (140.3 g) and octanol (179.4 g) are stirred for 30 minutes. Titanium isopropoxide (1.87 g) is added to the slurry and the reaction mixture is heated. At circa 176°C, the mixture begins to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 17.7 g of water has been collected (circa 10.5 hours total reflux time). The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (2.4 g oxalic acid in 105 g water), then with water (116 ml), thirdly by a solution of sodium carbonate in water (5.76 g sodium carbonate in 113.8 ml water), followed by water (103.7 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of dihexyl tetrabromophthalate, hexyl octyl tetrabromophthalate, and dioctyl tetrabromophthalate in a circa 1:2:1 ratio, bromine content 46.4%.

EXAMPLE TWO
Hexyl octyl tetrabr mophthalate

Tetrabromomphthalic anhydride (424.6 g), sodium carbonate (0.25 g), n-hexanol (210.8 g) and octanol (88 g) are stirred for 30 minutes. Titanium isopropoxide (2.0 g) is added to the slurry and the reaction mixture is heated. At circa 176°C, the mixture begins to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 17 g of water has been collected (circa 16 hours total reflux time). The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (1.44 g oxalic acid in 100 g water), then with water (100 ml), thirdly by a solution of sodium carbonate in water (7 g sodium carbonate in 100 ml water), followed by water (100 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of dihexyl tetrabromophthalate, hexyl octyl tetrabromophthalate, and dioctyl tetrabromophthalate in a circa 9:6:1 ratio.

EXAMPLE THREE
Hexyl decyl tetrabromophthalate

Tetrabromomphthalic anhydride (421.4 g), sodium carbonate (0.60 g), n-hexanol (140.1 g) and decanol (217.1 g) are stirred for 20 minutes. Titanium isopropoxide (1.6 g) is added to the slurry and the reaction mixture is heated. At circa 180°C, the mixture begins to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 19.6 g of water has been collected (circa 10 hours total reflux time). The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (5.5 g oxalic acid in 206 g water, 101.7 g of this solution used), then by a solution of sodium carbonate in water (9.5 g sodium carbonate in 218.3 ml water, 110.1 g of solution used), followed by water (103 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of dihexyl tetrabromophthalate, hexyl decyl tetrabromophthalate, and didecyl tetrabromophthalate in a 1:2:1 ratio, bromine content 44.9%.

EXAMPLE FOUR
Hexyl dodecyl tetrabromophthalate

Tetrabromomphthalic anhydride (419.3 g), sodium carbonate (0.60 g), n-hexanol (141 g) and dodecanol (251.5 g) are stirred for 20 minutes. Titanium isopropoxide (1.8 g) is added to the slurry and the reaction mixture is heated. At circa 180°C. the mixture begins to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 19.3 g of water has been collected (circa 10 hours total reflux time). The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (5.5 g oxalic acid in 206 g water, 108 g of this solution used), then by a solution of sodium carbonate in water (9.5 g sodium carbonate in 218.3 ml water, 117.6 g of solution used), followed by water (119.7 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of dihexyl tetrabromophthalate, hexyl dodecyl tetrabromophthalate, and didodecyl tetrabromophthalate in a 1:2:1 ratio, bromine content 42.6%.

EXAMPLE FIVE
Octyl decyl tetrabromophthalate

Tetrabromomphthalic anhydride (2057 g), sodium carbonate (1.28 g), 1-octanol (1296.9) and 1-decanol (525.2 g) were stirred for 30 minutes in a four neck round bottom flask fitted with mechanical stirrer, stopper, temperature controller, and Barrett trap. Titanium isopropoxide (8.7 g) was added to the reactor was heated to reflux. The reactor was heated at reflux until 91.6 g water was collected in the Barrett trap (circa 9.5 hours). Excess alcohol was removed first under reduced pressure (9.5 torr) to a maximum pot temperature of 172° C, then by adding water (530 ml) at 210 torr and circa 130° C pot temperature. The reaction mixture was treated with carbon (31.8 g) and diatomaceous earth (32.8 g) for 1 hour and then filtered through additional diatomaceous earth to give a mixture of dioctyl tetrabromophthalate, octyl decyl tetrabromophthalate, and diocytyl tetrabromophthalate, 2733 g in a 9:6:1 ratio.

EXAMPLE SIX
Octyl dodecyl tetrabromophthalate

Tetrabromomphthalic anhydride (421.5 g), sodium carbonate (0.61 g), n-octanol (180.5 g) and dodecanol (253 g) are stirred for 20 minutes. Titanium isopropoxide (1.7 g) is added to the slurry and the reaction mixture is heated. At circa 207°C, the mixture begins to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 20.4 g of water has been collected (circa 10 hours total reflux time). The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (2.77 g oxalic acid in 122 g water), then by a solution of sodium carbonate in water (4.73 g sodium carbonate in 114 ml water), followed by water (113.5 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of dioctyl tetrabromophthalate, octyl dodecyl tetrabromophthalate, and didodecyl tetrabromophthalate in a 1:2:1 ratio, bromine content 40.7%.

EXAMPLE SEVEN
1-Decyl 1-dodecyl tetrabromophthalate

Tetrabromomphthalic anhydride (421 g), sodium carbonate (0.60 g), n-decanol (218.5 g) and dodecanol (249.1 g) are stirred for 30 minutes. Titanium isopropoxide (1.5 g) is added to the slurry and the reaction mixture is heated to reflux and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reaction mixture is cooled to about 60° C and washed first with an oxalic acid water mixture (2.43 g oxalic acid in 105.6 g water), then by water (109 g) followed by a solution of sodium carbonate in water, and then by water (109.8 ml). The excess alcohol is removed on a wiped film evaporator at 180°C and 1 torr pressure to give the final product as a mixture of didecyl tetrabromophthalate, decyl dodecyl tetrabromophthalate, and didodecyl tetrabromophthalate in a 1:2:1 ratio.

EXAMPLE EIGHT
2-Ethylhexyl 1-hexyl tetrabromophthalate

In a 4-neck, 1L round bottomed flash equipped with mechanical stirrer, Barrett trap, reflux condenser, and temperature controller was placed 417 gm (0.90 mole) of tetrabromophthalic anhydride (PHT-4). To this was added 2-ethylhexanol (2-EHA, 175.8 gm 1.35 mole, 1.5 eq.), 1-hexanol$_3$ (138.0 gm, 1.35 mole, 1.5 eq.) and sodium carbonate (0.58 gm, 0.005 mole) and the mixture was stirred for 30 minutes. At this time, titanium (IV) isopropoxide (1.72 gm, 0.006 mole, 0.0068 eq.) and the reaction mixture was heated to reflux for 8 hours (top temperature was 210°C). Water was removed as it was formed. At this time, the reaction mixture was cooled to 60°C and washed with a solution of oxalic acid (2.4 gms in 100 mL of water), then water (100 mL), then sodium carbonate (1.0 gm in 100 mL of water) and finally water again 100 mL). The resulting viscous liquid was stripped on a wipe film evaporator (0.6 torr, 170°C, 3 mL/min feed) to give 623 gm (92% yield). The resulting product was mixed with carbon (6.23 gm) and heated to 110°C for one hour and then filtered through Celite to yield a water white material as a mixture of dihexyl tetrabromophthate, hexyl 2-ethylhexyl tetrabromophthalate and di-2-ethylhexylphthalate in a 1:2:1 ratio. OBr: 47.1 calc; 47.0 act.

EXAMPLE NINE
2-Ethylhexyl 1-octyl tetrabromophthalate

In a 4-neck, 1L round bottomed flash equipped with mechanical stirrer, Barrett trap, reflux condenser, and temperature controller was placed 417 gm (0.90 mole) of tetrabromophthalic anhydride (PHT-4). To this was added 2-ethylhexanol (2-EHA, 175.8 gm 1.35 mole, 1.5 eq.), 1-octanol$_3$ (175.8 gm, 1.35 mole, 1.5 eq.) and sodium carbonate (0.58 gm, 0.005 mole) and the mixture was stirred for 30 minutes. At this time, titanium (IV) isopropoxide (1.72 gm, 0.006 mole, 0.0068 eq.) and the reaction mixture was heated to reflux for 8 hours (top temperature was 225°C). Water was removed as it was formed. At this time, the reaction mixture was cooled to 60°C and washed with a solution of oxalic acid (2.4 gms in 100 mL of water), then water (100 mL), then sodium carbonate (1.0 gm in 100 mL of water) and finally water again 100 mL). The resulting viscous liquid was stripped on a wipe film evaporator (0.6 torr,

170°C, 3 mL/min feed) to give 642 gm (91% yield). The resulting product was mixed with carbon (6.42 gm) and heated to 110°C for one hour and then filtered through Celite to yield a water white material as a 1:2:1 mixture of dioctyltetrabromophthalate, octyl 2-ethylhexyl tetrabromophthalate, and di-2-ethylhexyl tetrabromophthalate.. OBr: 45.3 calc; 44.9 act.

EXAMPLE TEN
2-Ethylhexyl 1-decyl tetrabromophthalate

In a 4-neck, 1L round bottomed flash equipped with mechanical stirrer, Barrett trap, reflux condenser, and temperature controller was placed 417 gm (0.90 mole) of tetrabromophthalic anhydride (PHT-4). To this was added 2-ethylhexanol (2-EHA, 175.8 gm 1.35 mole, 1.5 eq.), 1-decanol$_3$ (214 gm, 1.35 mole, 1.5 eq.) and sodium carbonate (0.58 gm, 0.005 mole) and the mixture was stirred for 30 minutes. At this time, titanium (IV) isopropoxide (1.72 gm, 0.006 mole, 0.0068 eq.) and the reaction mixture was heated to reflux for 8 hours (top temperature was 242°C). Water was removed as it was formed. At this time, the reaction mixture was cooled to 60°C and washed with a solution of oxalic acid (2.4 gms in 100 mL of water), then water (100 mL), then sodium carbonate (1.0 gm in 100 mL of water) and finally water again 100 mL). The resulting viscous liquid was stripped on a wipe film evaporator (0.6 torr, 170°C, 3 mL/min feed) to give 653 gm (89% yield). The resulting product was mixed with carbon (6.53 gm) and heated to 110°C for one hour and then filtered through Celite to yield a water white material as a 1:2:1 mixture of didecyltetrabromophthalate, 2-ethylhexyl 1-decyl tetrabromophthalate, and di-2-ethylhexyl tetrabromophthalate.. OBr: 43.6 calc; 43.3 act.

EXAMPLE ELEVEN
2-Ethylhexyl 1-dodecyl tetrabromophthalate

In a 4-neck, 1L round bottomed flash equipped with mechanical stirrer, Barrett trap, reflux condenser, and temperature controller was placed 417 gm (0.90 mole) of tetrabromophthalic anhydride (PHT-4). To this was added 2-ethylhexanol (2-EHA, 175.8 gm 1.35 mole, 1.5 eq.), 1-dodecanol$_3$ (252 gm, 1.35 mole, 1.5 eq.) and sodium carbonate (0.58 gm, 0.005 mole) and the mixture was stirred for 30 minutes. At this

time, titanium (IV) isopropoxide (1.72 gm, 0.006 mole, 0.0068 eq.) and the reaction mixture was heated to reflux for 8 hours (top temperature was 260°C). Water was removed as it was formed. At this time, the reaction mixture was cooled to 60°C and washed with a solution of oxalic acid (2.4 gms in 100 mL of water), then water (100 mL), then sodium carbonate (1.0 gm in 100 mL of water) and finally water again 100 mL). The resulting viscous liquid was stripped on a wipe film evaporator (0.6 torr, 170°C, 3 mL/min feed) to give 653 gm (86% yield). The resulting product was mixed with carbon (6.53 gm) and heated to 110°C for one hour and then filtered through Celite to yield a water white material as a 1:2:1 mixture of di-1-dodecyltetrabromophthalate, 2-ethylhexyl 1-dodecyl tetrabromophthalate and di-2-ethylhexyltetrabromophthalate. OBr: 42.1 calc; 41.8 act.

EXAMPLE TWELVE
Tetradecyl tetrabromophthalate

In a 4-neck, 1L round bottomed flash equipped with mechanical stirrer, Barrett trap, reflux condenser, and temperature controller was placed tetrabromophthalic anhydride (690 g), tetradecyl alcohol (876 g), and sodium carbonate (0.51 g). The reactor was heated to 150° C overnight. Titanium isopropoxide (6.0 g) was added and the reaction mixture was heated to 215-218° C under 40 torr pressure. The pressure was slowly lowered to circa 10 torr while maintaining reflux. The reaction was heated at greater than 200° C for about 8 hours. The Barrett trap was replaced with a distilling head and receiver. The reactor was cooled to 150° C and a vacuum of circa 1 torr was applied and excess alcohol was removed by distillation (maximum pot temperature of 178° C). The reactor was cooled to 100° C, calcium carbonate (2.0 g) was added. Water (160 ml) was slowly added to the reactor over 3 hours, a vacuum of 19-20 inches of mercury was applied, and the pot temperature maintained at 110-120° C. The reactor was cooled to 100° C carbon (18.8 g) was added, and the mixture allowed to stir over the weekend. Diatomaceous earth (14.6 g) was added and the reactor stirred for 30 minutes. The contents were filtered through additional diatomaceous earth at 100° C to give a liquid which solidified upon standing. The material was ground in a mortar and pestle to give a white solid (1100 g).

EXAMPLE THIRTEEN
Octyl decyl tetrabromophthalate

Tetrabromomphthalic anhydride (417 g), sodium carbonate (0.26 g), n-octanol (88 g) and n-decanol (320.5 g) are stirred for 20 minutes. Titanium isopropoxide (1.75 g) is added to the slurry and the reaction mixture is heated and a water-alcohol mix is collected in a Barrett trap. The mixture is held at reflux and the water separated from the reactor via the Barrett trap. The reactor is heated until about 20.5 g of water has been collected (circa 9 hours total reflux time). The reaction mixture is cooled to about 60 °C and washed first with an oxalic acid water mixture (2.4 g oxalic acid in 100 g water), then with water (100 g), then by a solution of sodium carbonate in water (1.2 g sodium carbonate in 104 ml water), followed by water (150 ml). The excess alcohol is removed on a wiped film evaporator at 180 °C and 1 torr pressure to give the final product as a mixture of di-1-octyl tetrabromophthalate, 1-octyl-1-decyl tetrabromophthalate, and di-1-decyl tetrabromophthalate in a 1:6:9 ratio.

EXAMPLE FOURTEEN
Octyl decyl tetrabromophthalate

Tetrabromophthalic anhydride (2514 g), sodium carbonate (1.63 g), 1-octanol (1057 g) and 1-decanol (1289.6 g) were stirred at room temperature for 45 minutes in a four neck round bottom flask fitted with mechanical stirrer, stopper, temperature controller, and Barrett trap. Titanium isopropoxide (11.1 g) was added and the reactor was heated to reflux. The reactor was heated at reflux until 106.9 g water was collected in the Barrett trap (circa 8.5 hours). Excess alcohol was removed in a wiped film evaporator at 0.4 torr and a jacket temperature of 185 °C. Water was then added (50 g) followed by sodium carbonate (45 g) and the material heated at 90 °C for one hour. Excess water was stripped under reduced pressure and the temperature raised to 110 °C. The mixture was treated with carbon (38 g) and diatomaceous earth (39 g) for one hour and then filtered through additional diatomaceous earth to give a mixture of dioctyl tetrabromophthalate, octyl decyl tetrabromophthalate, and dioctyl tetrabromophthalate in a 1:2:1 ratio.

EXAMPLE FIFTEEN
Hexyl dodecyl tetrabromophthalate

Tetrabromophthalic anhydride (2613 g), sodium carbonate (1.63 g), 1-hexanol (1301 g) and 1-dodecanol (818.2 g) were stirred at room temperature for 45 minutes in a four neck round bottom flask fitted with mechanical stirrer, stopper, temperature controller, and Barrett trap. Titanium isopropoxide (17.1 g) was added and the reactor was heated to reflux. The reactor was heated at reflux until 139 g water was collected in the Barrett trap (overnight). Excess alcohol was removed in a wiped film evaporator at 0.5 torr and a jacket temperature of 190 °C. Water was then added (36 g) followed by sodium carbonate (36 g) and the material heated at 90 °C for one hour. Excess water was stripped under reduced pressure and the temperature raised to 110 °C. The mixture was treated with carbon (39.6 g), magnesium silicate (37 g) and diatomaceous earth (38 g) for one hour and then filtered through additional diatomaceous earth to give a mixture of dihexyl tetrabromophthalate, hexyl dodecyl tetrabromophthalate, and didodecyl tetrabromophthalate in a circa 9:6:1 ratio.

EXAMPLE SIXTEEN
Octyl dodecyl tetrabromophthalate

Tetrabromophthalic anhydride (2589 g), sodium carbonate (1.63 g), 1-octanol (1650 g) and 1-dodecanol (784 g) were stirred at room temperature for 45 minutes in a four neck round bottom flask fitted with mechanical stirrer, stopper, temperature controller, and Barrett trap. Titanium isopropoxide (13.5 g) was added and the reactor was heated to reflux. The reactor was heated at reflux until 123 g water was collected in the Barrett trap (circa 8 hours). Excess alcohol was removed in a wiped film evaporator at 0.5 torr and a jacket temperature of 190 °C. Water was then added (33 g) followed by sodium carbonate (30 g) and the material heated at 95 °C for one hour. Excess water was stripped under reduced pressure and the temperature raised to 110 °C. The mixture was treated with carbon (33.7 g), magnesium silicate (33 g) and diatomaceous earth (30 g) for one hour and then filtered through additional diatomaceous earth to give a mixture of dioctyl tetrabromophthalate, octyl dodecyl tetrabromophthalate, and didodecyl tetrabromophthalate in a circa 9:6:1 ratio.

EXAMPLE SEVENTEEN
Dodecyl tetrabromobenzoate

Tetrabromophthalic anhydride (664 g), 1-dodecanol (440 g), and sodium carbonate (6.1 g) were heated to 120 °C and transferred into hot (197-213 °C) 1-dodecanol (138 g). After the transfer was complete, the reaction mixture was heated under reduced pressure (5" of vacuum) for 9 hours. The reaction mixture was cooled to about 70 °C, water added and the two phases separated. The excess alcohol was removed on a wiped-film evaporator at 185 °C and 0.4 torr. The material was treated with carbon (12 g) overnight at 100 °C. Filter aid (12.8 g) was added and the material filtered at 105 °C to give a yellow liquid which solidified upon cooling to give a circa 2:1 mixture of dodecyl tetrabromobenzoate and dodecyl tetrabromophthalate.

EXAMPLE EIGHTEEN
Decyl tetrabromobenzoate

Tetrabromophthalic anhydride (905 g), decanol (883 g) and sodium carbonate (5.2 g) were heated to 196 °C and maintained there for about 8 hours. The mixture was then heated to 210 °C under reduced pressure (circa 20") for 3 hours. Excess alcohol was removed on a wiped film evaporator at 185 °C and 0.5 torr. The crude material was heated at 90 °C for two hours with carbon (19 g) and filter aid (30 g). The material was filtered at 90 °C to give a yellow solution which solidified upon cooling to give the product (670 g) as a circa 2:1 mixture of decyl tetrabromobenzoate and didecyl tetrabromophthalate.

EXAMPLE NINETEEN
Octyl decyl tetrachlorophthalate

Tetrachlorophthalic anhydride (1732 g), 1-octanol (2007 g) and 1-dodecanol (960.2 g) were heated to 135 °C and titanium isopropoxide (12.2 g) were heated at reflux for about 6 hours while collecting water in a Barrett trap. Excess alcohol was removed on a wiped-film evaporator (180-190 °C, 0.1 torr). Water (41.8 g) and sodium carbonate (28.4 g) were added and the material was heated to 90 °C for one hour. The water was removed under reduced pressure. Carbon (31 g), magnesium

silicate (30 g) and filter aid (30 g) were added and the mixture heated to 110 °C. Water was removed under reduced pressure and the mixture filtered hot to give a very light yellow solution of dioctyl tetrachlorophthalate, octyl decyl tetrachlorophthalate, and didecyl tetrachlorophthalate. This material was mixed in a 1:5 weight ratio with the material from Example Sixteen.

EXAMPLES TWENTY THROUGH TWENTY-SEVEN

Example Formulations: Simple formulation

phr = Parts Per Hundred Resin

A stainless steel blender was employed to mix PVC (Geon 102 EP, 100 phr), tribasic lead (5 phr), lubricant (stearic acid, 0.3 phr) and the flame retardant plasticizer (50 phr) at low speed for two minutes followed by high speed for two minutes. The material was heated in a vented oven to a flux temperature of 100° C. The material was removed from the oven and immediately mixed in the blender until the mixture was homogenous and fluffy. The material was placed on two roll mill heated to 360° F, mixed by cutting and removing the sheeted material and the mixed material added back to the mill in a 45° shift for 10 minutes. The sheeted PVC composite was removed from mill to cool and cut with shears into 3 to 4 sheets 2" x 4" to equal circa 40 grams combined weight per sheet. The sheets were placed in a .065" rectangular mold which was covered on each side with Teflon sheeted fabric. The PVC composite, mold and fabric were placed between two preheated (360°C) stainless steel plaques approximately 12" x 12".

The plaques were placed in a heated compression molder preheated to 360° C and pressed for five minutes at 25 tons on a 8" ram. The stainless steel plaques containing the PVC composite were removed from the heated press, immediately placed in a cooling press using city tap water for cooling, and pressed at 20 tons on 8" ram. The PVC composite sample was removed, cut into samples, and analyzed by Dynamic Mechanical Analysis ("DMA"). DMA is used to determine the viscoelastic properties of plastics. In the most typical mode of operation, a sinusoidal strain of defined amplitude is applied to the sample at a selected frequency, specified strain

amplitude in the 0.3-0.5 mm range and a 1-20 Hz frequency range. The sample is cooled to the desired temperature (-150° C is the lower limit) and a sample is heated at a controlled rate, typically 3-4°/min. The DMA instrumentation constantly monitors the phase relationship between the applied strain and the resultant stress, a change rubbery behavior to a brittle, glass behavior. Storage modulus, loss modulus and tan δ are determined.

Ingredients (Phr)	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27
Base Resin	100	100	100	100	100	100	100	100
Tribasic Lead	5	5	5	5	5	5	5	5
Lubricant	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
FR Plasticizer	Product from Example 3	Product from Example 5	Product from Example 9	Product from Example 14	Product from Example 15	Product from Example 16	Product from Example 13	Di-2-ethylhexyl Tetrabromo phthalate
Physical State of FR	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid/solid mix	Liquid
Glass Transition Temp 50 parts, °C	-21.1	-33.2	-10.8	-38.3	-25.3	-39.5	-42.6	-8.9
Glass Transition Temp 100 parts, °C	-51	-64.3	-45.2	-66.2	-59.5	-60.4	-72.6	-43.9

EXAMPLES TWENTY-EIGHT THROUGH THIRTY-TWO (THIRTY-TWO IS COMPARATIVE)

The process set forth in examples 20-27 was generally followed, provided, however that the following data was obtained using low mass clamps during the Dynamic Mechanical Analysis. This data cannot be directly compared with data is examples 20-27. Lower mass clamps give better sensitivity and return lower values of transition temperatures than the higher mass clamps.

Ingredients (Phr)	Example 28	Example 29	Example 30	Example 31	Comparative Example 32
Base Resin	100	100	100	100	100
Tribasic Lead	5	5	5	5	5
Lubricant	0.3	0.3	0.3	0.3	0.3
FR Plasticizer	Example 17	Example 18	Example 19	Example 5 + Di 2-ethylhexyl Tetrachlorophthalate (5:1)	Di 2-ethylhexyl Tetrabromophthalate
Physical State of FR	Solid	Solid	Liquid	Liquid	Liquid
Glass Transition Temp 50 parts, °C	-84	-54	-52	-51	-36

EXAMPLES THIRTY-THREE (COMPARATIVE), THIRTY-FOUR AND THIRTY-FIVE

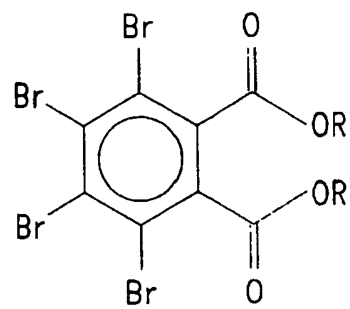
PVC (Geon 102 EP, 85 parts), CPVC (15 parts), tribasic lead (10 phr, Topanol CA (0.2 phr), stearic acid (0.2 phr), dibasic lead (0.2 phr) Aristowax 165 (0.2 phr), a selected flame retardant plasticizer (40 phr), and diocytl sebacate (5 phr) were mixed in a stainless steel blender at low speed for two minutes then at high speed for two minutes. The material was heated in a vented oven to a flux temperature of 100° C. The blend was removed from the oven and immediately mixed in the blender until the mixture was homogenous and fluffy. AOM (25 phr), ATH (45 phr) and LSFR Antimony oxide were added to the beaker and mixed an additional 2 minutes. The composite was mixed on a two roll mill heated to 360° F by cutting and removing the sheeted material and adding it back to the mill in a 45° shift for 2 minutes. Elvaloy 341 was added to the composite sheet in a even distribution and the composite sheet was mixed for an additional eight minutes. The sheeted PVC composite was removed from the mill to cool and then cut with shears into 2" x 4" (3 to 4 sheets, approximately 40 grams weight). The PVC composite was placed in a 0.065" rectangular mold, covered on each side with Teflon sheeted fabric, and placed between two stainless steel plaques approximately 12" x 12". The stainless steel plaques are preheated to 360° F. The plaques were placed in a heated compression molder preheated to 360° C, and pressed for five minutes at 24 tones on a 8" ram. The stainless steel plaques were removed from the heated press and immediately placed in a cooling press using city tap water for cooling, and pressed at 20 tons on 8" ram. The PVC composite sample was removed and cut into samples that were analyzed by DMA.

	Example 33 (comparative)	Example 34	Example 35
GEON102EP	85 Parts	85 Parts	85 Parts
CPVC	15 Parts	15 Parts	15 Parts
Elvaloy 741	12 phr	12 phr	12 phr
Tribasic Lead	10 phr	10 phr	10 phr
AOM	35. phr	25. phr	25. phr
ATH	45. phr	45. phr	45. phr
Topanol CA	0.2 phr	0.2 phr	0.2 phr
Stearic Acid	0.2 phr	0.2 phr	0.2 phr
Dibasic Lead	0.2 phr	0.2 phr	0.2 phr
Aristowax 165	0.2 phr	0.2 phr	0.2 phr
F/R Plasticizer	dioctyl-substituted tetrabromophthalate 40 phr	Example 5 40 phr	Example 14 40 phr
Dioctyl Sebacate	5.0 phr	5.0 phr	5.0 phr
LSFR Antimony Oxide	3.0 phr	3.0 phr	3.0 phr
Normal Linear Carbonations	12	8.5	9.0
DMA Onset Storage Modulus °C	-57	-64	-61
DMA Peak Storage Modulus °C	-33	-41	-40

phr = Parts Per Hundred Resin

What is claimed is:

1. A flame retardant plasticizer composition, comprising a first tetrabromophthalate ester having the formula:



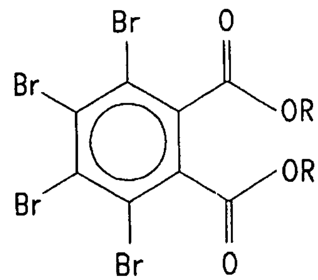
wherein R is a first linear alkyl chain of from about 5 to about 16 carbons;
wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons;
wherein R' is different than R; and
wherein the total number of carbons in R and R' is greater than 12.

2. The composition according to claim 1, wherein one of R and R' is a hexyl chain and the other of R and R' is selected from the group consisting of an octyl chain, a decyl chain and a dodecyl chain.

3. The composition according to claim 1, wherein one of R and R' is an octyl chain and the other of R and R' is selected from the group consisting of a decyl chain and a dodecyl chain.

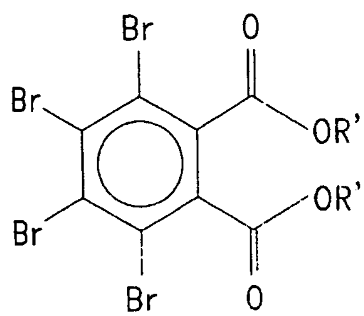
4. The composition according to claim 1, wherein one of R and R' is a decyl chain and the other of R and R' is a dodecyl chain.

5. The composition according to claim 1, further comprising:
a second tetrabromophthalate ester having the formula:



and;

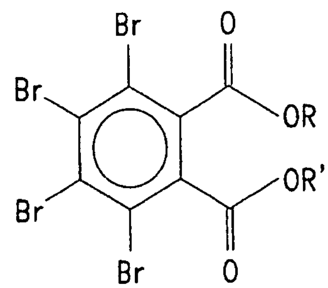
a third tetrabromophthalate ester having the formula:



6. The composition according to claim 1, wherein the plasticizer further comprises a tetrachlorophthalate ester.

7. The composition according to claim 6, wherein the tetrachlorophthalate ester is 2-ethylhexyltetrachlorophthalate.

8. A flame retardant plasticizer composition, comprising a first tetrabromophthalate ester having the formula:



wherein R is a first linear alkyl chain of from about 5 to about 16 carbons;

wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons;

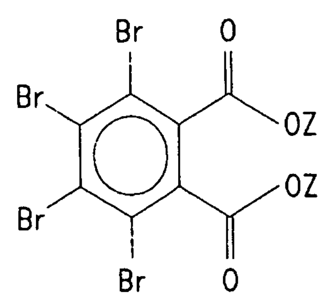
wherein R' is different than R; and

wherein one of R and R' comprises at least seven carbons.

9. The composition according to claim 8, wherein the plasticizer further comprises a tetrachlorophthalate ester.

10. The composition according to claim 9, wherein the tetrachlorophthalate ester is 2-ethylhexyltetrachlorophthalate.

11. A flame retardant plasticizer composition, comprising a tetrabromophthalate ester having the formula:



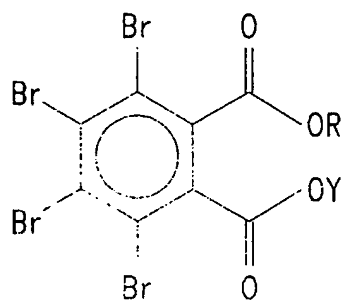
wherein Z is a linear alkyl chain of from about 14 to about 16 carbons.

12. The composition according to claim 11, wherein Z is a tetradecyl chain.

13. The composition according to claim 11, wherein the plasticizer further comprises a tetrachlorophthalate ester.

14. The composition according to claim 13, wherein the tetrachlorophthalate ester is 2-ethylhexyltetrachlorophthalate.

15. A flame retardant plasticizer composition, comprising a tetrabromophthalate ester having the formula:



wherein R is a linear alkyl chain of from about 5 to about 16 carbons; and wherein Y is a branched alkyl chain of from about 5 to about 16 carbons.

16. The composition according to claim 15, wherein Y is an ethylhexyl chain; and

wherein R is selected from the group consisting of a hexyl chain, an octyl chain, a decyl chain and a dodecyl chain.

17. The composition according to claim 15, wherein the plasticizer further comprises a tetrachlorophthalate ester.

18. The composition according to claim 17, wherein the tetrachlorophthalate ester is 2-ethylhexyltetrachlorophthalate.

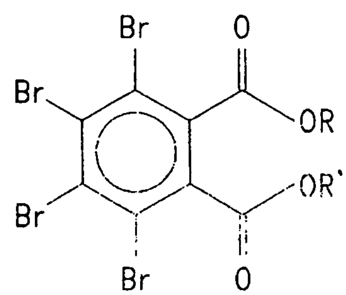
19. A formulation comprising:

a polyvinyl chloride;

a heat stabilizer;

a lubricant; and

a composition comprising a tetrabromophthalate ester having the formula:



wherein R is a first linear alkyl chain of from about 5 to about 16 carbons;

wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons;

wherein R' is different than R; and

wherein the total number of carbons in R and R' is greater than 12.

20. The formulation in accordance with claim 19, wherein the heat stabilizer is selected from the group consisting of tribasic lead sulfate, dibasic lead phthalate, dibasic lead phosphite, lead sulfophthalate, dibasic lead phthalate, and basic lead sulfophthalate.

21. The formulation in accordance with claim 19, wherein the lubricant is selected from the group consisting of stearic acid, blend of paraffin wax and calcium, stearate, and paraffin wax.

22. The formulation in accordance with claim 19, further comprising chlorinated polyvinyl chloride.

23. The formulation in accordance with claim 19, further comprising a smoke suppressant.

24. The formulation in accordance with claim 23, wherein the smoke suppressant is selected from the group consisting of ammonium octamolybdate and zinc molybdate.

25. The formulation in accordance with claim 19, further comprising a filler material.

26. The formulation in accordance with claim 25, wherein the filler material is selected from the group consisting of alumina trihydrate, calcined aluminum silicate, and electrical grade clay.

27. The formulation in accordance with claim 19, further comprising antimony trioxide.

28. The formulation in accordance with claim 19, further comprising a UV stabilizer.

29. The formulation in accordance with claim 28, wherein the UV stabilizer is selected from the group consisting of hindered amine light stabilizers and UV absorbers.

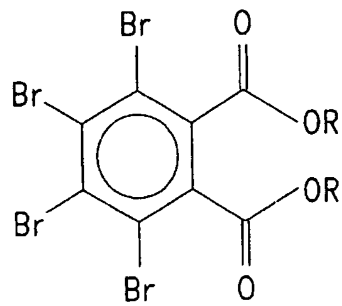
30. A formulation comprising:

a polyvinyl chloride;

a heat stabilizer;

a lubricant; and

a composition comprising a tetrabromophthalate ester having the formula:



wherein R is a first linear alkyl chain of from about 5 to about 16 carbons;

wherein R' is a second linear alkyl chain of from about 5 to about 16 carbons;

wherein R' is different than R; and

wherein one of R and R' comprises at least seven carbons.

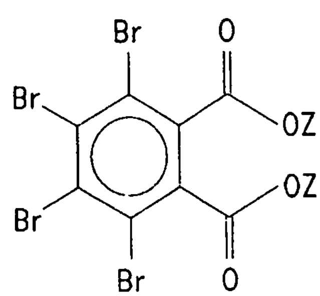
31. A formulation comprising:

a polyvinyl chloride;

a heat stabilizer;

a lubricant; and

a composition comprising a tetrabromophthalate ester having the formula:



wherein Z is a linear alkyl chain of from about 14 to about 16 carbons.

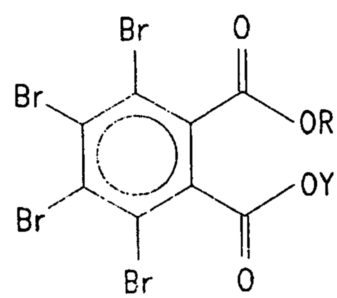
32. A formulation comprising:

a polyvinyl chloride;

a heat stabilizer;

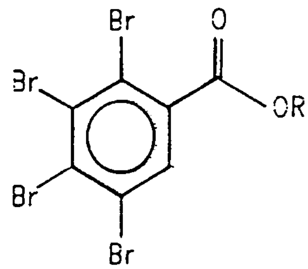
a lubricant; and

a composition comprising a tetrabromophthalate ester having the formula:



wherein R is a linear alkyl chain of from about 5 to about 16 carbons; and wherein Y is a branched alkyl chain of from about 5 to about 16 carbons.

33. A flame retardant plasticizer composition, comprising a first tetrabromobenzoate ester having the formula:



wherein R is an alkyl chain of from about 5 to about 16 carbons.

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(54) Title: NOVEL FLAME RETARDANT PLASTICIZERS

(57) Abstract

The present invention provides novel esters synthesized from organic alcohols and tetrahalophthalic anydride or tetrahalophthalic acid, processes to make such esters, and novel uses of these esters. The invention provides three Groups of dialkyltetrahalophthalate compositions which exhibit surprisingly advantageous features, including excellent plasticizing functionality and low smoke generation. The esters may be symmetrical, in that both alcohols of the ester are the same, or they may be unsymmetrical with both alcohols of the derived phthalate ester different, or they may be mixtures of symmetrical and unsymmetrical esters. Inventive esters are useful as flame-retardant plasticizers in PVC or other polymeric systems.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,298,517 A (SANDLER) 03 November 1981, columns 3-4.	1-33
X	US 5,049,697 A (BOHEN et al.) 17 September 1991, columns 10-14.	1-33
X	US 5,393,820 A (ASHWORTH et al.) 28 February 1995, columns 2-4.	1-33
X,P	US 5,728,323 A (DAY et al.) 17 March 1998, columns 2-5.	1-33

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